

Kinetics of Conformer Reactions. I. A New Approach

Klimovitskii E., Shtyrlin Y., Kashaeva E., Kiselev V., Vafina R., Khotinen A.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

A new approach to determination of partial rate constants for reactions of conformers is developed on the basis of constituents of the Gibbs energy of activation for reactions of a series of conformationally heterogeneous substrates. Unlike classical Winston-Holness (Eliel) procedure, the proposed model allows solving of formal kinetics tasks under conditions of thermodynamic control and in the absence of diastereoisomeric products. The p values and partial rate constants were determined for the chair and twist conformers of a series of 2-substituted 1,3-dioxacyclohept-5-enes in the model Diels-Alder reaction with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate in two solvents. In dioxane the chair conformer reacts 3.4 times, and in acetone, 1.4 times faster than does the twist conformer. The different reactivities of the conformers are due to effects of the medium in combination with stereoelectronic orbital interactions in the transition state.
